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PROCEDURE AND EQUIPMENT FOR DETERMINATION OF CO_2 CONCENTRATION IN GASES

[Verfahren und Vorrichtung zur Bestimmung des CO_2 – Gehaltes in Gasen]

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Description

The invention is with reference to the determination of CO_2 concentration in gases with at least one metal oxide gas sensor.

Metal oxide gas sensors are mixed gas sensors which reveal gaseous reactions which are caused due to specific surface, temperature, volume and geometric variations. The metal oxides gas sensors which can be generated from thin film techniques show a high thermodynamic stability of their active layers even at very high temperatures. The frequently used SnO2 in addition provides a high stability against moisture and is resistant to a large number of alkalis and acids. All these factors point to the fact that metal oxide gas sensors can be used in multiple areas and are recommended for making continuous measurements in office and household appliances and can also be employed in environment analytics. With the help of suitably built sensor switches and through the use of sensor arrays which are combined with intelligent signal processing devices, further possibilities could be explored and sensitivity, selectivity and drift suppression could be achieved. With the types of gas sensors known so far, which are produced on metal oxide bases,

gaseous components such as CO_x, NO_x, CH_4, C_2H_5OH, H_2 and NH_3 can be analyzed without any problems. The detection of CO_2 however poses serious problems although it is of great interest in environmental sciences. The determination of CO_2 concentration is very important as a result of the high CO_2 emissions, which lead to the so called Greenhouse effect. Therefore, there is a relatively increased need for developing cost effective sensors. The metal oxide gas sensors therefore show advantages over other sensors based on different measurement principles since they can be built for the specific gas components based on changing the contact geometry, choice of doping elements and catalysts.

Up till now the catalysts employed and the materials used in the gas sensors for increasing the sensitivity of CO_2 measurement varied. Suggestions for the same were made by Hoefer, U., Kuhner, G., Schweizer, W., Sulz, G. and Steiner, K., "CO and CO_2 Thin film SnO_2 Gas sensors on Si Substrates*", Sensors & Actuators B22 (1994), pages 115 – 119, Hanada, M., Koda, H., Onaga K., Onouchi, T., "Development of CO_2 sensor using Lanthanum Doped Tin Dioxide Semiconductor Gas Sensor*", Kongressband Sensor

95, 7. Internal Fachmesse mit Kongress for Sensoren, Messaufnehmer & Systeme, Nurnberg, 9th to 11th May 1995, Pages 445 – 450, and Haeusler, A., and Meyer, J – U, "Thick film – CO_2 sensor based on conductivity changes of a special metal gas oxide mixture", Kongressband Sensor 95, 7. Internal Fachmesse mit Kongress fur Sensoren, Messaufnehmer & Systeme, Nurnberg, 9th to 11th May 1995, Pages 427 – 432.

With the techniques described so far, it is not possible to increase the sensitivity of measurements even with a choice of good catalysts in order to measure the CO_2 concentration using metal oxide gas sensors with a satisfactory degree of accuracy.

The objective of this invention is therefore to find possibilities of utilizing metal oxide gas sensors to determine the CO_2 concentration to a satisfactory degree of accuracy.

The objective has been achieved in this invention as per the process described in claim 1 and the equipment described in claim 14. Advantageous designs and further extensions of the innovative solution can be achieved with the application of the characteristics mentioned in the claims.

In the case of known metal oxide gas sensors, changes in the electrical conductivity occurring as a result of influence of the various gas components is used.

Thereby, the sensitive thin film is used as a resistance element which creates a change in conduction when in contact with the gas to be analyzed. Thereby, a change in the conductivity is created through a reversible reaction of the gas constituents to be analyzed and the surface of the boundary layer of the sensor. The charge carrier exchange in the active film of the sensors can accordingly be either increased or decreased so that a change in the conductivity is brought about. Thus, the presence of different gas constituents can be ascertained. The sensor can be influenced by the usage of different catalysts, usage of different doping substances, variations in the working temperature, characteristics of the contact method, sensor construction, and measurement methods used and also the size and geometry of the sensory active surfaces. The currently known metal oxide gas sensors show limited sensitivity towards CO_2 and the improvements suggested so far are not sufficient to obtain a satisfactory level

of sensitivity. The signal pattern of the known sensors is too small and is not sufficient for any industrial application.

With the help of the innovative procedure and a suitably built device, those signal patterns can be retained, which are clearly increased and can be significantly recorded during the interference reactions.

The gas flow which is to be analyzed in this innovative method is partially moistened and the wet gas flow is measured with the help of a metal oxide gas sensor – preferably a SnO_2 – Sensor.

It can therefore be advantageous to split the gas flow into a measurement branch and a reference branch. The gas in the measurement branch is to be analyzed with reference to CO_2 content after the corresponding gas flow has been dehumidified.

The gas flow that has been passed through the reference branch can be passed through at least one sensor without dehumidifying in order to compensate for cross sensitivity/interference since CO_2 can be measured with enough significance only in the dehumidified gas. Similarly in the reference branch, metal oxide gas sensors or other sensors such as electrochemical cells, GaAs – gas sensors, gas FETs, pellistors, integrated

optical sensors, quartz and/or spectrometers could be used.

Apart from the parallel arrangement of both the measurement branches, there could also be a serial arrangement of the branches. Thereby, at least another gas constituent is recorded with a suitable sensor before dehumidifying. Finally, a suitable dehumidifier is attached to the metal oxide gas sensor with which the concentration of CO_2 can be recorded.

Several suitable methods could be employed for the dehumidification. The dehumidification could be achieved through cooling the gas flow. Further, it is also possible to use dehumidifiers which contain hygroscopic materials which can remove the moisture content of the gas flow to the required extent. Suitable membranes need to be used for the dehumidification process which is impermeable for water and water vapor.

It is also advantageous that at the end of the dehumidification process, the residual moisture of the gas which is to be analyzed is observed using humidity measurement equipment and hence variations in moisture content could be compensated.

In a similar manner, the influence of temperature can

be controlled with the measurement of the gas temperature.

For the compensation of temperature variations that keep occurring, there is a possibility of considering a heating system for the corresponding gas flow in order to maintain the temperature within a desired range.

If the gas flow to be analyzed is split into two branches and carried through two different lines, it would be advantageous to regulate the corresponding volume or mass flow.

The following explains the invention in detail with the help of an example:

Fig. 1. Shows a schematic diagram of the equipment as per the invention

Fig. 2. Shows a diagram with the recorded CO_2 concentration in the case of different residual moisture contents and

Fig. 3. Shows a diagram with time dependent CO_2 concentrations which are measured in the case of 0% moisture content by using different sensors.

In the case of the equipment designed and built as shown in Figure 1, the gas flow to be analyzed would be passed through two lines 3 and 4 which are arranged next to each other whereby the gas flowing through line 3 is made to pass through a dehumidifier device 2 before it reaches a metal oxide gas

sensor 1 which is preferably a SnO_2 sensor.

In line 4 which is arranged in parallel to line 3, there is another sensor 5 with which at least one other gas constituent is analyzed. There could also be multiple sensors 5 in line 4 which can record multiple gas components and be based on other measurement principles. The so measured values could be used to remove any interference in the measurements.

In this example, there is a temperature sensor 6 and a humidity measurement device 7 in the dehumidifier 2. In both cases the so measured values can be used for a corresponding temperature and moisture content compensation of the values measured using the metal oxide gas sensor 1. A reference has been avoided in the shown diagram of the example.

Apart from the possibility of the arrangement of the lines 3 and 4 in parallel, there could also be an innovative arrangement in which the sensor(s) 5 could be arranged before the dehumidifier 2 in the direction of flow of the gas to be analyzed and, the CO_2 concentration is measured using the metal oxide gas sensor 1 which is at the end of the dehumidifier device.

The range of measured values showed in fig 2 show the reactions of a SnO_2 – Thin film sensor with different concentrations of CO_2 which are determined in different residual moisture gases and given in % terms. It can be clearly seen that even in the case of 0% relative moisture content, significant measured values within the MAK – values (5000 ppm) can be measured.

The diagram shown in figure 3 gives the CO_2 pulse of 5000 ppm measured with the help of three different sensors in synthetic air with 0% moisture of gas flow to be analyzed. Sensor 1 was Antimony doped and sensors 2 and 3 were Palladium doped SnO_2 sensors.

The measurement characteristics showed in figures 2 and 3 shows clearly that satisfactory signal strengths could be measured with the help of this innovative procedure which ensure a high level of accuracy with respect to CO_2 content in the gas to be analyzed.

Patent claims

1. Procedure for determination of CO_2 concentration in gases with the help of at least one metal oxide gas sensor whereby at least one of the gas streams to be analyzed is passed through a dehumidifier.

2. Procedure as per claim 1 means that the gas to be analyzed has at the most 10% of moisture content

3. Procedure as per claim 2 means that the gas has at least 5% moisture content

4. Procedure as per claims 1 to 3 means that the gas flow is divided into two streams and one of the streams is passed through a dehumidification device and then passed through a metal oxide gas sensor.

5. Procedure as per claim 4 means that the part of the gas flow which is not dehumidified is passed over at least one additional sensor

6. Procedure as per claims 1 to 3 means that the non dehumidified gas to be analyzed is passed over at least one sensor, then dehumidified and passed over a metal oxide gas sensor.

7. Procedure as per at least one of the above claims 1 to 6 means that the gas stream which is not dehumidified is analyzed using at least another sensor based on a different measurement principle in order to reduce the interference to a minimum.

8. Procedure as per at least one of the above claims 1 to 7 means that the gas stream is

dehumidified through a cooling device.

9. Procedure as per at least one of the above claims 1 to 8 means that the moisture content of the gases would be measured and kept under consideration during the determination of the CO_2 content.

10. Procedure as per at least one of the above claims 1 to 9 means that the temperature of the gases would be measured.

11. Procedure as per at least one of the above claims from 1 to 10 means that the variation in moisture and temperature would be compensated.

12. Procedure as per at least one of the above claims 1 to 11 means that the gas stream would be heated.

13. Procedure as per at least one of the above claims 1 to 12 means that the mass flow and volume flow of the gases would be regulated.

14. Equipment for carrying out the procedure as per claim 1 means that there is at least one dehumidifier (2) before the metal oxide gas sensor (1) in the direction of flow of gas to be analyzed.

15. Equipment as per claim 14 means that the metal oxide (1) gas sensor is a SnO_2 sensor.

16. Equipment as per claims 14 and 15 means that the divided gas streams flow through separate lines (3) whereby the line (4) carries non-dehumidified gas which can be analyzed with the help of another sensor (5)

17. Equipment as per claim 16 means that at least one more gas constituent could be determined with the help of the sensor(s) 5.

18. Equipment as per claims 15 and 16 means that the sensor(s) (5) is an infra red sensor, an optical sensor, an electrochemical cell, a GaAs-sensor, a Gas-FET, a Pellistor sensor, a quartz sensor and/or a spectrometer.

19. Equipment as per at least one of the claims 14 to 18 means that the dehumidifier (2) contains hygroscopic material.

20. Equipment as per at least one of the claims 14 to 18 means that the dehumidifier (2) contains a cooling system or has one attached to it.

21. Equipment as per at least one of the claims 14 to 18 means that the dehumidifier (23) contains a membrane that prevents passage of water or water vapor through it.

22. Equipment as per claim 14 means that the sensor(s) (5) are arranged before the

dehumidifier (2) in the direction of flow of gas which is to be analyzed.

23. Equipment as per at least one of the claims 14 to 22 means that the gas stream has at least one temperature sensor (6) arranged in it.

24. Equipment as per at least one of the claims 14 to 23 means that a humidity sensor (7) is attached to a dehumidifier (2).

25. Equipment as per at least one of the claims 14 to 24 means that there is a system for heating the gas.
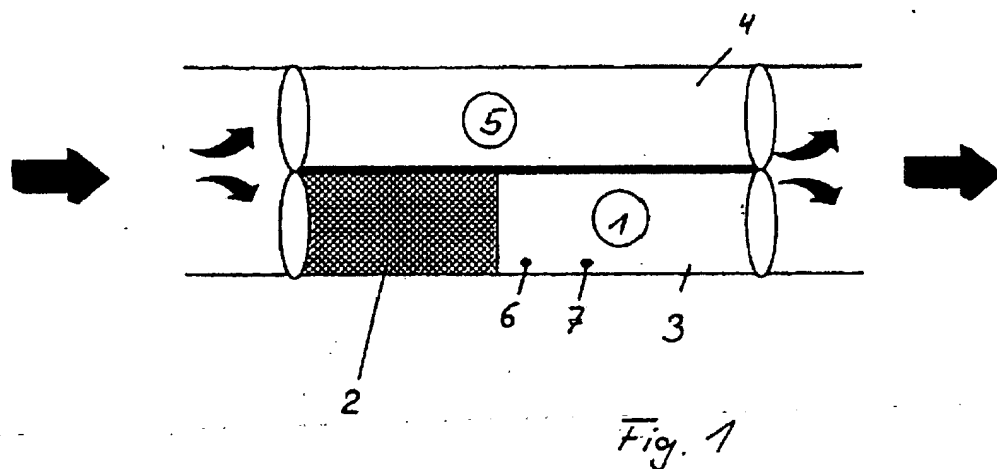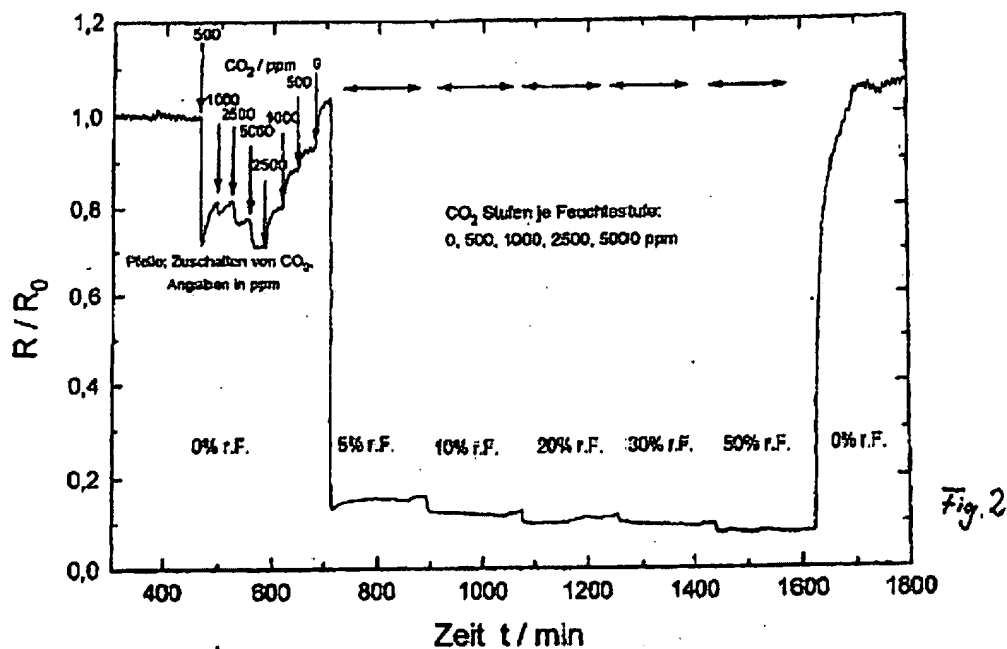

Attached - 3 pages of diagrams

Fig. 1

Figure: 1

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Figure: 2

Fig. 2

CO₂ levels based on moisture content:
0.500, 1000, 2500, 5000 ppm
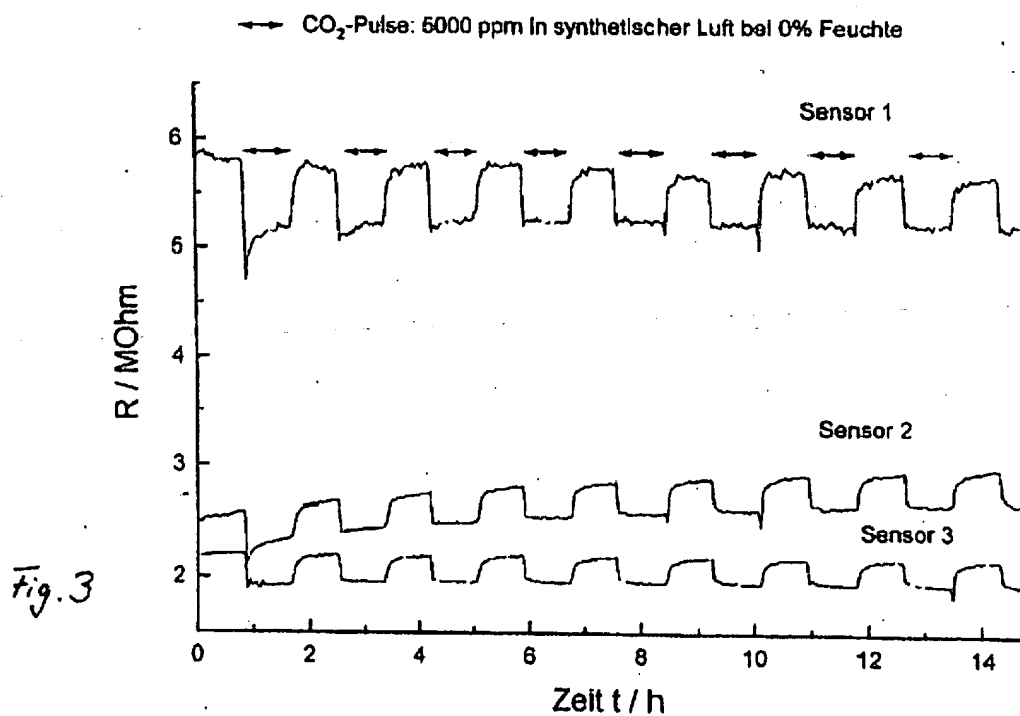

Arrow: Commission of CO₂
Details in ppm

R/R₀

Time t/h

CO₂ – pulse: 5000 ppm in synthetic conditions with 0% moisture

Sensor 1

Figure: 3

CO₂-Pulse: 5000 ppm in synthetischer Luft bei 0% Feuchte

Fig.3

R/MOhm

Sensor 2

Sensor 3

Time t/h

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